

MODERATE TEMPERATURE COAL HYDROGENATION

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INTRODUCTION

A well-defined correlation among coal structure, the reaction conditions of liquefaction, and the composition of the products is an important fundamental objective of coal liquefaction research. This objective has been very elusive because of the great complexity of the coal structure and because of the many side reactions that occur at commercial liquefaction temperatures. Such side reactions include thermal fragmentation, and the condensation or polymerization of reactive intermediates, which result in gas and coke formation.

Additional complications are caused by the use of a donor solvent in most coal liquefaction processes. The donor solvent interferes with the investigating of the reaction chemistry and analyzing of the reaction products by forming adducts with the coal-derived intermediates. Furthermore, it is difficult to characterize separately the donor solvent and its derivatives in the complex product mixture. At moderate reaction temperatures, internal hydrogen rearrangement may play a relatively more significant role in radical stabilization. Consequently, hydrogenating coal with gas-phase hydrogen and without a donor solvent offers significant advantages in understanding the mechanisms that occur.

The reaction of coal with H_2 has been investigated in the temperature range of 400 to 500°C (1). At these temperatures, however, cracking and condensation reactions that lead to gas and coke formation are fast and take place indiscriminately. The objective of this research was to explore hydrogenation at lower temperatures where the thermal side reactions are less extensive.

EXPERIMENTAL

The hydrogenation experiments were conducted in a 1-liter stirred autoclave equipped with a liner and a specifically designed anchor-type impeller. It is essential to use a properly designed impeller in this reaction to improve gas-solid contact and mass transfer, particularly during the initial softening of the coal particles, when caking can occur. A liner made of Inconel 600 and an impeller made of 316 SS were used in Experiments 1A through 1E and in Experiment 2. The liner and impeller were coated with glass for Experiments 3 and 4 to eliminate the catalytic effect of the metal surface. In each experiment, 25 g of high volatile bituminous coal was used. The coal was ground to -200 mesh and dried at 115°C in vacuo before use.

Two sets of hydrogenation experiments were conducted using two bituminous coals of slightly different rank. The objective of the first set was to investigate reactions in the 275 to 325°C range using 1-h and 48-h reaction times. The objective of the second set was to explore the effect of coal rank and two catalysts on coal conversion and product oil characteristics. Reaction parameters were selected on the basis of the results of the first set of experiments.

The first set was conducted using a Pittsburgh seam bituminous coal of the following composition (% daf): C:80.1, H:5.1, S:3.6, N:1.6, and O:9.6. The dry coal contained 11.2% ash. The second set was conducted at 325°C using reaction times of 48 h. A Pittsburgh seam bituminous coal of somewhat higher rank was used in these experiments. The elemental composition of this coal (% daf) was as follows: C:82.1, H:5.9, S:3.3, N:1.6, and O:7.1. The ash content of the dry coal was 8.2%.

Each experiment was conducted at a hydrogen pressure of approximately 20.7 MPa. After the product gases had been measured and analyzed, the hydrogenated product was Soxhlet-extracted with benzene. The benzene solution was concentrated by distillation and then poured into excess hexane to precipitate the asphaltenes. After filtration, the hexane solution was distilled and the hexane evaporated to recover the oil fraction. The benzene-insoluble residue was Soxhlet-extracted with THF and separated into a THF-soluble fraction and an insoluble residue. This procedure was based on a separation method recommended by Mima et al (2). The solvent-separated fractions were analyzed for elemental composition. A detailed characterization of the product oils was made using simulated distillation, vapor phase osmometry, field ionization mass spectrometry (FIMS), and proton nuclear magnetic resonance (NMR) spectrometry.

RESULTS AND DISCUSSION

The test conditions and product yields of the first set of experiments are presented in Table 1. Very little reaction was observed by visual inspection or chemical analysis in a 1-n reaction period at the lowest test temperature (275°C). The appearance of the dry powder product very closely resembled that of the starting coal. Most of the gas products consisted of carbon oxides; the gaseous hydrocarbon (CH₄) yield was only 0.04%. Compared with the starting coal, the amount of the THF-soluble extract increased from 5% to 8%. Some of these results have been presented elsewhere (3).

An experiment made using D₂ under the same conditions (1B), however, showed that a significant H-exchange had taken place at 275°C. About 15% of the protium (¹H) in the coal was replaced by deuterium (²H or D). In this experiment, a sizable increase in the THF solubility also was observed. At 310 to 325°C, the product was a shiny black solid, and there were significant increases in the THF solubility. Finally, when the reaction time was increased to 48 h at 325°C, the THF solubility of the product increased to 77%. Of this amount, 72% was hexane-soluble oil (daf coal basis). The fraction of gaseous products increased only slightly as the temperature was increased from 275 to 325°C, and the reaction time increased from 1 h to 48 h. This indicates that the product liquids were stable under these experimental conditions. The structural characterization of the product oil from this last experiment at 325°C for 48 h is discussed below.

The product yields from the second set of experiments (2 through 4) are listed in Table 2. These experiments were designed to test the effect of coal rank and two selected catalytic conditions on coal conversion and product oil characteristics. Table 2 also includes the product yields from the lower rank coal (Experiment 1E) for comparison. The product yields from Experiments 1E and 2 show that the lower rank coal used in Experiment 1E was much more reactive, particularly with regard to the conversion of the asphaltenes to oil.

The evaluation of Experiments 2 and 3 shows that the autoclave's metal surfaces have a strong catalytic effect on oil production. The results of Experiment 4 indicate that nickel very effectively catalyzes the conversion of coal to soluble products but is somewhat less effective than the autoclave surfaces in catalyzing oil production. Gas formation was remarkably low in every experiment. It appears that gas formation is proportional to oil production; the gas yield was approximately 10% of the oil yield in each experiment.

The elemental composition of the oil products is given in Table 3. The H/C atomic ratios varied from 1.13 to 1.24, and the oil from the nickel-catalyzed reaction had the highest value. The oil produced from lower rank coal (Experiment 1E) had the same H/C ratio as the oil product from the higher ranking coal (Experiment 2), even though the oil yield in Experiment 1E was 50% higher. The oil from Experiment 1E had a significantly lower oxygen content than the oil from Experiment 2. This difference may indicate that the cleavage of certain C-O bonds has an important role in oil formation.

The hydrogen-type distributions of the oil products were determined by proton NMR spectroscopy. Figure 1 shows the spectrum of the oil from Experiment 1E as an example. The integration results are presented in Table 4. In agreement with the elemental analysis data, the NMR integration values show that the oil made by nickel catalysis (Experiment 4) had significantly more saturated structures than the oil formed via catalytic effect of the autoclave surfaces (Experiment 2). These results plus the fact that the oil yield was greater in Experiment 2 than in Experiment 4 indicate that the catalytic effect of the autoclave surfaces preferentially catalyzed hydrocracking reactions leading to oil formation, while nickel catalysis resulted in more hydrogen uptake leading to the formation of saturated structures.

The oil products from Experiments 2 through 4 were further characterized by simulated distillation and by FIMS. The data indicate that there is close similarity between the structural features of the oils from Experiments 2 and 3. The presence of several homologous series (such as alkyl derivatives of phenol, diphenyl/acenaphthene, and pyrene) has been indicated in these oil products. The product oil from the nickel-catalyzed hydrogenation is quite different in that the data indicated the presence of more hydrogenated ring structures in it.

The hydrogen type distributions of an oil fraction obtained by moderate temperature hydrogenation and of distilled oil fractions of extract and process solvent samples from an integrated two-stage liquefaction pilot plant, are compared in Table 5. The oil from moderate temperature hydrogenation is much less aromatic and contains more saturated structures than the pilot plant products, which were produced at significantly higher temperatures.

SUMMARY AND CONCLUSIONS

Hydroliquefaction of two bituminous coals was explored to obtain information on the chemistry of liquefaction. Tests were conducted in the temperature range of 275 to 325°C and at 20.7 MPa hydrogen pressure. No donor solvent was added to the reactant to simplify product analysis and the evaluation of the results. The results and conclusions are summarized below:

1. Exploratory tests showed that at a liquefaction temperature of 325°C, high conversion to oil can be obtained with few side reactions resulting in gas or coke formation. Therefore, this temperature was selected to explore further the effect of coal rank and catalysis on coal conversion.

2. Of the two bituminous coals tested, the lower rank coal (C = 80%) was much more reactive and gave 50% higher oil yield than the higher rank coal (C = 82%). The oil yields were 72% and 48%, respectively.
3. It was shown in experiments made with the higher rank coal (C = 82%) that the metal components of the autoclave (liner and impeller) had a strong catalytic effect on the liquefaction reaction. When the metal parts of the autoclave were replaced with a glass-coated liner and impeller, the oil yield was reduced from 48% to 19%.
4. Catalysis by nickel, applied as nickel acetate impregnated into the coal, gave significantly different results from those obtained in the metal-lined reactor. Overall conversion to soluble products was higher using the nickel catalyst (94% versus 87%). However, nickel catalysis gave lower conversion to oil (40% versus 48%).
5. The oil produced in the nickel-catalyzed hydrogenation was significantly more aliphatic in character than the product from the metal-surface catalyzed reactions. The aliphatic to aromatic proton ratios were 83/17 and 74/26, respectively. Also, the nickel-catalyzed product had a much higher $(\beta + \gamma)/\alpha$ aliphatic proton ratio than the metal-catalyzed product (55/28 versus 43/32). These data indicate that nickel catalysis strongly promoted hydrogenation of aromatic rings while the metal components more effectively catalyzed hydrocracking reactions, which resulted in oil formation.

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TABLE 1
TEST CONDITIONS AND PRODUCT YIELDS

Experiment	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (% daf Coal)		Product Appearance
				Gas	THF Soluble	
Untreated coal	-	-	-	-	5	Dry powder
1A	272	20.0	1.0	0.4	8	Dry powder
1B (D ₂)	271	20.3	1.0	0.3	15	Dry powder
1C	310	20.7	1.0	1.0	22	Black solid
1D	325	19.3	1.0	1.7	29	Shiny black solid
1E	325	19.3	48.0	5.8	77 ^a	Thick dark oil

^aMost of this THF-soluble product was hexane-soluble oil (72% based on daf coal).

TABLE 2
PRODUCT DISTRIBUTIONS FROM MODERATE TEMPERATURE
LIQUEFACTION EXPERIMENTS^{a,b}

Experiment	1E	2	3	4
Coal rank	80	82	82	82
% C, daf				
% O daf	9.6	7.1	7.1	7.1
Catalyst	Yes (Liner/ impeller)	Yes (Liner/ impeller)	No	Yes (Nickel- acetate)
Conversion	84	87	80	94
Product yields:				
Gas	6	4	3	4
Oil	72	48	19	40
Asphaltene	6	18	33	28
Preasphaltene	1	17	25	22
Residue	16	13	20	6

^aAll hydrogenation experiments made at 325°C, ~20 MPa, and using 48-h reaction time.

^bPercent on loss-free, daf-basis.

TABLE 3
ELEMENTAL COMPOSITIONS OF PRODUCT LIQUIDS

Sample	Composition (wt. %)						H/C
	C	H	N	O	S	Total	
Experiment 1E, oil	88.2	8.4	1.1	1.8	0.6	100.1	1.14
Experiment 2, distilled liquid	86.3	8.1	1.2	3.6	0.4	99.6	1.13
Experiment 2, oil	86.1	8.2	0.9	4.2	0.4	99.8	1.14
Experiment 3, oil	87.2	8.6	0.8	2.7	0.7	100.0	1.18
Experiment 4, oil	86.5	8.9	0.9	2.7	0.6	99.6	1.24

TABLE 4
PROTON NMR INTEGRATION VALUES

Hydrogen Type	Chemical Shift (ppm)	Experiment Number				
		Hydrogen-Type Distribution (%)				
		1E (Oil)	2 (Liquid)	2 (Oil)	3 (Oil)	4 (Oil)
Condensed aromatic, 4+ rings	7.85	4.0	2.5	3.1	1.5	1.4
Condensed aromatic, 2-3 rings	7.2-7.85	10.1	10.4	10.5	7.7	6.4
Aromatic single ring	6.8-7.2	4.7	6.7	6.6	6.8	5.4
Phenolic OH	6.3-6.8	1.4	5.2	7.2 ^a	2.8	3.1
α^2 -aliphatic	3.7-4.2	1.8	2.1	0.9	1.1	0.6
α -aliphatic	2.0-3.7	33.9	30.7	29.7	32.3	28.5
β -aliphatic	1.0-2.0	35.4	34.4	33.2	36.9	39.3
γ -aliphatic	0.5-1.0	8.7	8.0	8.8	10.9	15.3

^aIncludes 2.3% contribution from 4.2 to 5.2-ppm region.

TABLE 5
MODERATE TEMPERATURE VS TWO-STAGE LIQUEFACTION-COMPARISON
OF HYDROGEN TYPES

Oil Product From	Yield (%)	Hydrogen Distribution (%)				
		Condensed Aromatic	Single Ring Aromatic	Aliphatics		
				α	β	γ
Moderate temperature liquefaction ^a	72	14	6	36	35	9
Two-stage liquefaction ^b Extract ^c	41	27	14	28	29	4
Process solvent ^c	48	26	10	24	35	3

^aPittsburgh seam coal, C = 80.1%

^bIllinois No. 6 coal, C = 79.2% (from Ref. 4)

^c-454°C distillate

